

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN THE APPLICATION OF:

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TITLE: DIESEL LUBRICANT LOW IN SULFUR AND PHOSPHORUS
Wickliffe, Ohio

Hon. Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R. §1.132

I, Virginia A. Carrick, declare as follows:

I received a bachelor of science degree with a major in chemistry in 1986 from John Carroll University. I have been employed by The Lubrizol Corporation since 1987 as a chemist. Since 1992 I have been responsible for formulating lubricants for various engines including stationary gas, heavy duty diesel, passenger car, compressed natural gas, and 4 stroke motorcycle engines. I am one of the inventors in the above-mentioned application, and I am familiar with the references which were used in the rejection thereof.

In order to illustrate the improvement in performance of the compositions of the above invention, the following experiments were performed under my direction:

Lubricant formulations were prepared closely duplicating Example 1 of the Fetterman reference, US 5,102,566, as reported in greater detail in the table below. The example designated "F Ex 1" is a comparative example that corresponds closely to the

CERTIFICATE OF EFS SUBMISSION (37 C.F.R. § 1.8(a)(1)(C))

I hereby certify that this Declaration is being filed electronically via the USPTO EFS to the Commissioner for Patents, United States Patent & Trademark Office, in accordance with §1.6(a)(4) on:

August 13, 2008
Date of Deposit

/Nancy S. Dedek/
Deposited by: Nancy S. Dedek

example in Fetterman. I also had prepared a similar sample, "F Ex 1," for reference, modified somewhat to contain a lower amount of zinc dialkyldithiophosphate (ZDDP) and thus a lower level of phosphorus.

Fetterman's example differs from the materials of the present invention in (at least) two respects. First, a sulfur-containing material is present in Fetterman's example, in particular, a sulfurized alkyl phenol antioxidant, which is not an element of the present invention: rather, the present invention requires a sulfurized olefin antiwear agent. Second, the sulfated ash level (ASTM D 874) of Fetterman is lower, in particular, about 0.44, versus 0.6 and above or 0.8 and above for the present invention. (Also, it appears to me likely that the total phosphorus level in Fetterman's example is greater than the maximum of 0.1 percent of the present invention, although this is difficult to determine with certainty from the information Fetterman provides.) In order to evaluate the effect of these variables, I prepared, first, reference examples Ref A and Ref C, reported in the table below, each of which have a higher sulfated ash level of about 0.80 to 0.88. The sulfated ash was increased by addition of 1 wt.% of an overbased calcium alkylbenzenesulfonate detergent, which is a very common component used in engine lubricant formulations. Then, from Ref A and Ref C, the sulfurized alkyl phenol antioxidant was removed and replaced by a sulfurized olefin antiwear agent, to provide Ex B and Ex D, respectively. The amount was selected to provide the same level of sulfur to the lubricant formulations.

Each of the lubricant formulations was tested for antiwear performance and coefficient of friction, and the results are shown in the Table below. The HFRR test refers to the "high frequency reciprocating rig" test, which is a friction and wear test developed as part of a performance evaluation of low sulfur and phosphorous crankcase formulations. This method has been shown to differentiate friction and wear performance of various friction modifiers, antiwear, and detergent chemistries. This method uses a ball-on-disk configuration to quantitatively measure wear and average friction coefficient of fully formulated crank case oils in a high frequency reciprocating rig. In the test, a steel ball and a steel disk are rubbed against each other under a 500 g load in a 1 mm reciprocating motion while submerged in heated (105 °C) sample for 75 minutes. The resulting scar is measured under 100x magnification. The oil is stressed with 1% cumene hydroperoxide.

The "4-Ball" test is a wear test described in ASTM D 4172, reporting similar properties as the HFRR test.

The HTCP (high temperature Cameron Plint) test is similar to the HFRR test except that it is conducted at a higher temperature, 150 °C, uses a stroke length of 2.5 mm and a load of 100 N.

Results are shown in the following table:

Example:	F Ex 1'	Ref A	Ex. B	F Ex 1	Ref C	Ex. D
Component ^a , weight %	(lower phosphorus)		(higher phosphorus)			
PIBSA-PAM disp'ts (58%) ^a	7.57	7.57	7.57	7.57	7.57	7.57
S'd alkylphenol antiox. (58%)	2.83	2.83		2.83	2.83	
Sulfurized olefin ^c (100%)			1.21 ^d			1.21 ^d
ZDDP (90%)	1.07	1.07	1.07	1.35 ^b	1.35	1.35
Overbased Mg sulfonate detergent (58%)	0.5	0.5	0.5	0.5	0.5	0.5
Overbased Ca sulfonate detergent (58%)		1.0	1.0		1.0	1.0
Viscosity index improver, olefin copolymer (13%)	8.2	8.2	8.2	8.2	8.2	8.2
Pour point depressant ^c (44%)	0.3	0.3	0.3	0.3	0.3	0.3
Base oil	balance	balance	balance	balance	balance	balance
Analytical Values						
TBN: measured (calculated)	5.3 (5.7)	8.3 (8.7)	8.3 (8.7)	5.5 (5.7)	8.3 (8.7)	8.3 (8.7)
% Sulfated Ash: measured (calculated)	0.45 (0.44)	0.80 (0.84)	0.82 (0.84)	0.52 (0.46)	0.88 (0.87)	0.88 (0.87)
% Phosphorus: measured (calculated)	0.075 (0.075)	0.076 (0.075)	0.080 (0.079)	0.096 ^b (0.095)	0.096 (0.094)	0.099 (0.099)
% Sulfur: measured (calculated)	0.334 (0.352)	0.356 (0.370)	0.346 (0.370)	0.370 (0.393)	0.394 (0.411)	0.399 (0.411)
Test Results						
HFRR, wear scar, μm	255	323	206	236	259	242
HFRR, friction coefficient	0.157	0.176	0.151	0.154	0.153	0.157
4-Ball, avg. scar diam, μm	430	430	420	n.d.	n.d.	n.d.
4-Ball, friction coefficient	0.133	0.144	0.126	n.d.	n.d.	n.d.
HTCP, wear scar, μm	398	519	332	n.d.	n.d.	n.d.
HTCP, friction coefficient	0.128	0.138	0.120	n.d.	n.d.	n.d.

a. Percent amount in parentheses after the components represents the % active ingredient, the balance, if any, being diluent oil.

b. The selection of this value assumes that the amount of the zinc dialkyldithiophosphate (ZDDP) in Fetterman's example 1 was 1.35 percent as reported in his table rather

than 1.45 percent as reported in the footnote to his table. This value also does not take into account the difference between volume percent and weight percent ZDDP (the specific gravity of ZDDP solution is 1.08 versus about 0.9 for mineral oil). Either of those changes alone would cause the value of %P in Fetterman's actual example 1 to exceed 0.1 percent.

c. An esterified styrene/maleic anhydride copolymer, conventionally present but not specifically reported to be included in Example 1 of Fetterman. In my experience and opinion, this component will have no measurable effect on wear test results.

d. Amount selected to provide the same level of sulfur to the composition as from the sulfurized phenol antioxidant.

e. Sulfurized 4-carbobutoxycyclohexene

n.d. = Not determined

Example "F Ex 1" corresponds closely to Example 1 of Fetterman, although the amount of phosphorus is most likely a bit lower than in his actual example, as described in footnote "b" to my table, above.

Example "Ex D" is an example corresponding to "F Ex 1," but modified to be within the scope of the present claims by (a) having a higher sulfated ash level of 0.88 (and correspondingly increased TBN), and (b) using a sulfurized olefin antiwear agent rather than Fetterman's sulfurized phenol antioxidant.

Example "Ex B" is a related example, which is further modified from "Ex D" to have a lower total phosphorus level of less than 0.09%, namely, about 0.08%, as in certain embodiments of the present invention.

The results show that Ex B, within the present invention, exhibits significantly improved antiwear performance compared with F Ex 1, and also reduced coefficient of friction, even though it uses much less of the ZDDP antiwear agent.

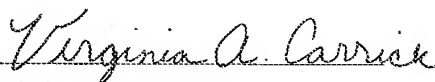
Ex D shows little change compared with F Ex 1, but in my opinion even this represents an unexpectedly good result. The mere fact of increasing the level of detergent (and thus TBN and sulfated ash) will have a deleterious effect on wear performance to begin with. This effect is evident from Ref C, which is identical to F Ex 1 except at higher TBN and sulfated ash. The wear scar value of 259 μm for Ref C is significantly worse than the value of 236 for F Ex 1. (A similar effect is seen by comparing Ref A with F Ex 1'.) Thereafter, replacing the sulfurized phenol antioxidant

with the sulfurized olefin antiwear agent reduces the wear scar significantly, to 242 μm , restoring it to the value in the lower ash formulation, even though the ash level is much higher.

A similar series of comparisons may be made with a lower phosphorus variant of Fetterman's Example 1. (A reduction in phosphorus, generally, without any corrective measures, will generally lead to higher wear.) Please see F Ex 1' (the lower phosphorus modification of Fetterman) along with Ref A and Ex B. Ex B is a direct comparison against F Ex 1', having been modified to meet the conditions of the present claims only by replacing the sulfurized alkylphenol antioxidant with sulfurized olefin and increasing the level of sulfated ash. These changes result in a significant reduction in wear scar by the HFRR, 4-Ball, and HTCP tests as well as a reduction in coefficient of friction. This improvement is despite the fact that the increase in sulfated ash, alone, leads to a significant worsening of these values (Ref A). The improvement in Ex B is particularly notable when compared against the original Fetterman example, F Ex 1.

I believe that the data shows that the use of sulfurized olefin (rather than sulfurized alkylphenol antioxidant) permits acceptable or improved antiwear performance to be obtained even at low phosphorus levels (ZPPD levels), that is, phosphorous levels equal to or lower than those employed in the Fetterman patent, and using moderately low sulfated ash formulations.

I further declare that all statements herein made of my own knowledge are true and all statements herein made on information and belief are believed to be true. I understand that willful false statements and the like are punishable by fine or imprisonment or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon.


Virginia A. Carrick

August 7, 2008 (date)